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Chitosan coating on silk fibroin for oil spill treatment

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A new kind of silk fibroin based oil sorbent has been developed by coating chitosan onto silk fibroin. The effect of chitosan coating on oil sorption and oil retention behavior of silk fibroin is studied. The maximum oil sorption capactiy of chitosan coated silk fibroin is 26.80 g/g and 19.46 g/g for engine oil and diesel oil respectively. SEM is used to analyze the surface morphology and FTIR confirms the chemical changes after chitosan treatment. Reusability test results suggest that after 5 cycles, the oil absorbency of chitosan coated silk fibroin is 14.39 g/g and 10.30 g/g against engine oil and diesel oil respectively. A comparison of oil sorption capacity of chitosan coated silk fibroin with other synthetic sorbents is also presented. It is concluded that chitosan coated silk fibroin has the potential to become widely employed sorbent for oil spill removal applications.

Keywords: Chitosan, Coated fibre, Oil sorbent, Oil spill, Silk fibroin

1 Introduction

Oil spill accidents occur regularly during production, storage and transportation of oil. When oil comes in contact with water, it forms emulsion or coating on water surface[1]. Coating of oil layer in a marine environment can adversely affect the aquatic ecosystem and the environment. Oil consists of several hydrocarbons, including polycyclic aromatic hydrocarbons and alkanes[1].

Therefore, to minimize the oil pollution hazard and recover the spilled oil simultaneously it is necessary to use a relatively efficient product. Till now, oil dispersants, oil spill skimmers, oil gelling agents and oil sorbents have been used for oil spill removal applications[2].

Sorbents are generally considered as most efficient for oil spill cleaning up applications. Sorbents can be categorized into three categories, viz inorganic mineral materials, synthetic organic polymer materials and natural organic materials[2]. The inorganic mineral materials contain organic clay, silica, fly ash graphite, zeolites, perlite and vermiculite. Synthetic organic polymer materials contain polypropylene, polyester, polyacrylate, polyethylene and polyurethane. Natural organic materials contains cotton, kapok, jute, banana, nettle, coir, silk, etc[3].

Natural fibre based sorbents are cost effective, biodegradable and sustainable. Considering these advantages, many researchers have begun to investigate the oil sorption behavior of several fibrous materials including cotton, kapok, jute, banana, nettle, coir, silk, etc. Though natural fibrous materials have several advantages, one of the major drawbacks is the poor oil sorption capacity. In order to improve the oil sorption capacity, natural fibres are usually subjected to several surface modification techniques including grafting, thermal carbonization, acetylation and coating with poly-n-butylmethacrylate (PBMA)/SiO_2[3]. On the other hand, the high cost and the complicated preparation process are the main factors that limit the commercial use of the technology. Hence, it is essential to find an environment-friendly, economical and readily prepared coating for producing oil sorbents from natural fibres.

Silk is biodegradable, biocompatible, mechanically strong and nontoxic polymeric materials that have been widely used for textile applications[4]. Due to the unique features of silk, now a day it has been investigated by several researchers for oil spill removal applications. Moriwaki *et al.*[5] investigated the oil sorption properties of silk worm cocoon waste. Aslanidou *et al.*[6] developed superhydrophobic-oleophobic silk sorbents through spray coating method by using SiO_2 nanoparticle dispersed solution. Chen *et al.*[7] used atomic layer deposition technique with TiO_2 nanoparticles for the preparation of hydrophobic silk sorbent. Patowary *et al.*[8] functionalized silk fibroin with ethanol based Octadecylamine (ODA) through solution based dip coating method.

Chitosan is a valuable non-toxic, biocompatible, and biodegradable natural polymer widely used in

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different application areas, such as waste water treatment, biomedicine, food packaging, etc. In addition to the features mentioned above, chitosan also shows prominent flocculating, chelating and adsorption effects[9]. Koseoglu[10] applied chitosan onto Luffa cylindrical fibre and studied the effects of chitosan coating on oil absorbency. The results showed that the oil absorbency is improved by 42% as compared to raw Luffa cylindrical fibre. In a very recent study, the sorption of oil from crude oil water emulsions was studied by using chitosan as biosorbent material. It is reported that the main parameters affecting the sorption are chitosan dosage, contact time, and initial crude oil concentration[11].

Previous studies showed that the effect of chitosan coating on the oil sorption behavior is not well reported in the literatures. Considering the advantageous features of chitosan, in the present work chitosan has been used as a coating on silk fibroin and the influence of chitosan coating on oil sorption behavior is studied.

2 Materials and Methods

2.1 Materials

Silk cocoons of *Bombyx mori* were received from Vadavalli Sericulture Farm, (Coimbatore, India). Chitosan of viscosity 300 cps and degree of deacetylation 0.82 was used for the study. The viscosity of engine oil and diesel oil used in this study were 280 cP and 110 cP respectively. The density of engine oil and diesel oil were 0.90 g/cm^3 and 0.82 g/cm^3 respectively. All other chemicals used were of analytical grade.

2.2 Methods

2.2.1 Nonwoven Development and Pretreatment

Silk cocoons of *Bombyx mori* as procured were cut into staple fibres of 50 mm length and used for the development of nonwovens fabrics. Nonwoven fabrics were prepared using DILO needle punching machine at PSG TECHS COE INDUTECH, Coimbatore, India. The silk fibres were opened and subsequently carded by means of roller carding machine. The nonwoven web was developed from the carded fibres using cross lapper. Punching density of 70 punches/cm^2 and needle penetration depth of 10mm were used to prepare nonwoven fabrics. The silk nonwoven fabrics having 220 g/m^2 weight and 2.2 mm thickness were developed and used for the subsequent process. Silk nonwoven fabrics were treated in an aqueous solution of 0.1% (w/v) sodium carbonate at 98º–100°C for 30 min to remove sericin[12]. Subsequently, silk nonwoven fabrics were washed repeatedly with water to remove sodium carbonate. Finally, the sample was dried for 12 h at 50 °C to obtain the dried silk fibroin nonwoven fabrics.

2.2.2 Coating of Silk Fibroin Nonwoven Fabrics

Chitosan solutions of different concentrations 0.5%, 1%, 1.5%, 2% and 2.5% (w/v) were prepared using 2.0% (v/v) aqueous acetic acid through stirring the dispersion for one hour at 60°C as reported earlier[12]. The silk fibroin nonwoven fabrics were then immersed in chitosan solutions of various concentrations at 30°C for 24 h. After chitosan coating, the silk fibroin nonwoven fabrics were washed three times with 0.1M sodium hydroxide solution followed by deionized water. Finally, the silk fibroin nonwoven fabrics were dried at 50 °C for 6 h.

2.2.3 SEM and FTIR Study

Surface morphology of silk fibroin and chitosan coated silk fibroin was studied using scanning electron microscope (Zeiss, Model EVO50). A gold coating was given to the samples.

The FTIR analysis of silk fibroin and chitosan coated silk fibroin were recorded using FTIR spectrophotometer (Shimadzu 8400s, Japan) by ATR sampling technique through recording 45 scans in % T mode in the range of 4000–600 cm^{-1}.

2.2.4 Determination of Oil Sorption Capacity and Oil Retention

The oil sorption behavior of the chitosan coated and uncoated silk fibroin nonwoven fabrics was determined according to ASTM F 716-09 standard. Dry silk fibroin nonwoven fabrics were separately immersed into engine oil and diesel oil for 15 min and then samples were taken out and hung for one minute. Subsequently, the weight (W_w) of wet silk fibroin nonwoven fabrics was measured. Engine oil sorption by chitosan coated silk fibroin nonwoven fabric is shown in Fig. 1. The oil sorption was determined using the below relationship:

$$\text{Oil sorption (g/g)} = [W_w\text{-}W_d/W_d]$$

where W_w and W_d are the weight of wet silk fibroin nonwoven fabrics and dry silk fibroin nonwoven samples respectively. All the tests were carried out for ten times and the average was taken.

A known mass of chitosan coated silk fibroin nonwoven fabrics was placed in 150 mL of oil for 15 min. The silk fibroin nonwoven fabrics was removed and vertically hung. The adsorbed oil begins to drop from the silk fibroin nonwoven fabrics. The weight of the material is measured after 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 and 240 s of drainage. Subsequently, the amount of oil retained in the nonwoven fabrics was determined .All the tests were carried out for ten times and the average was taken.

2.2.5 Reusability Test

The reusability of chitosan coated silk fibroin nonwoven fabrics was studied as per the process described previously[13]. Initially, the oil sorption capacities of chitosan coated silk fibroin nonwoven fabrics were measured and subsequently nonwoven samples were squeezed between a pair of two rollers at a pressure of 10 kgf/cm and reduction in weight of the nonwoven samples was measured. The squeezed nonwoven samples were again immersed in oil for 15 min and oil sorption capacity was measured[13]. The reusability capability of chitosan coated silk fibroin nonwoven fabrics was determined by measuring the oil sorption capacity of samples after repeated sorption and desorption cycles.

3 Results and Discussion

3.1 SEM Analysis

The surface morphology of silk fibroin and chitosan treated silk fibroin fabrics are analyzed using SEM and the results are shown in Fig. 2. It is observed that the surface is smooth for the silk fibroin as compared to chitosan treated silk fabrics. The chitosan treated silk fibroin fabrics clearly show the presence of variable amounts of particles on their surfaces and hence the fabric surface appears rougher.

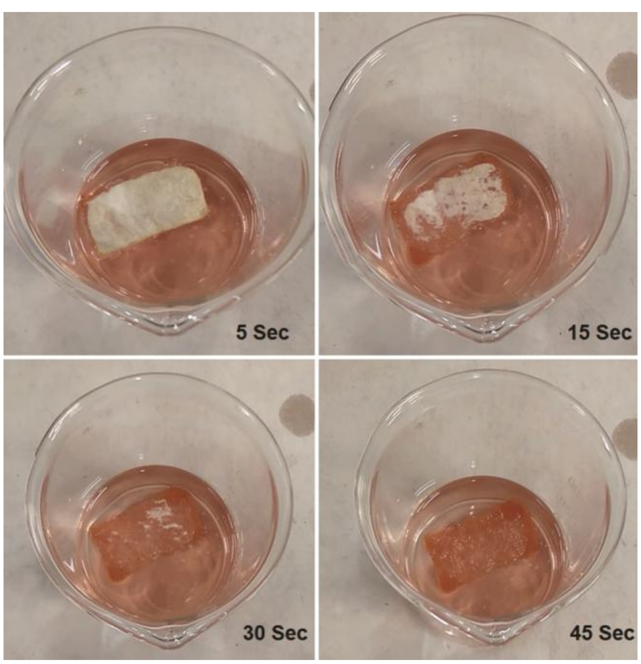

Fig. 1 — Engine oil sorption by chitosan coated silk fibroin nonwoven fabrics

3.2 FTIR Analysis

The FTIR analysis of silk fibroin and chitosan coated silk fibroin are recorded using FTIR spectrophotometer. The presence of broad peak from 3600 cm^{-1} to 3100 cm^{-1} is mainly attributed to the OH stretching and bending vibration mode in the molecule[14]. For silk fibroin fabrics, peak at 1610 cm^{-1} corresponds to amide I (C = O stretching vibration directly associated to the backbone conformation), peak at 1510 cm^{-1} corresponds to amide II (out of phase combination of the N–H bending and the C–N stretching), and peak at 1230 cm^{-1} corresponds to amide III (in phase combination of the N–H bending and the C–N stretching)[15]. In case of chitosan coated silk fibroin, the arrangement of all the amide bands are somewhat shifted as compared to silk fibroin fabrics. The shift of amide bands confirms the interactions between silk fibroin and chitosan. Possibly the interaction could be due to hydrogen bonds formation

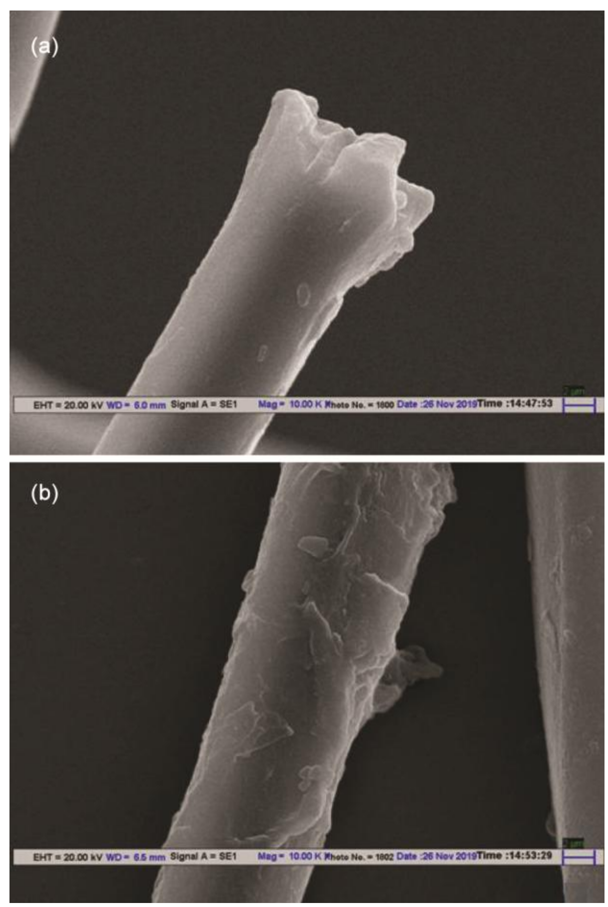

Fig. 2 — SEM micrographs of (a) silk fibroin and (b) chitosan coated silk fibroin

between NH and CO groups, which can shift the amide bands in FTIR spectra[14, 15].

3.3 Oil Sorption Capacity

Oil sorption and retention capacity are the two important characteristics of a material to be used as sorbent for oil/water separation[13]. The oil sorption capacity of the chitosan uncoated and chitosan coated silk fibroin sample against engine oil and diesel oil is shown in Fig. 3. It is observed that with the increase in chitosan concentration, the oil sorption capacity of silk fibroin increases up to a point and thereafter it decreases. At higher chitosan concentrations, more active sites will be available on sorbent for oil to be adsorbed at a faster rate, thus leading to a higher interaction between oil particles and adsorbent[10]. Beyond certain point, saturation of oil binding sites occurs, which reduces the oil uptake of the material.

The maximum oil sorption capactiy of chitosan uncoated silk fibroin is 14.32 and 10.29 g/g for engine oil and diesel oil respectively. These values are much lower than the sorption capacity of chitosan uncoated silk fibroin, which are 26.80 and 19.46g/g sorption for engine oil and diesel oil respectively. The high oil sorption capacity of the silk fibroin nonwovens is mainly due to the chitosan coating. The amine (NH_2) functional group of chitosan tends to attract anionic ions, namely OH^-. Electrostatic forces of attraction are present among this positive charge (amine group) on chitosan and the negative charge of fatty acids in oils[9]. Also by charge neutralization mechanism, chitosan a positively charged polymer could adsorb and destabilize the negatively charged colloids of residue oil[9]. Due to the above reasons, chitosan coated silk fibroin shows excellent oil sorption capacity against both engine oil and diesel oil. Oil droplet on chitosan coated silk fibroin (single fibre) is shown in Fig. 4.

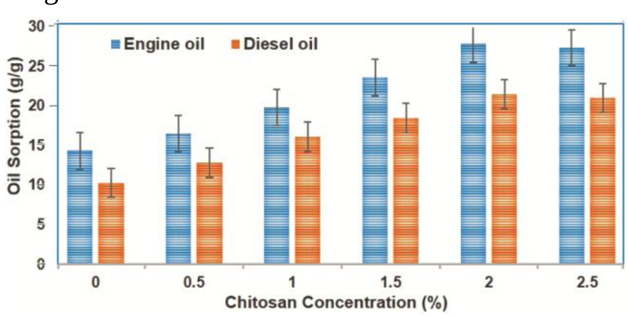

Fig. 3 — Oil sorption capacity of the silk fibroin

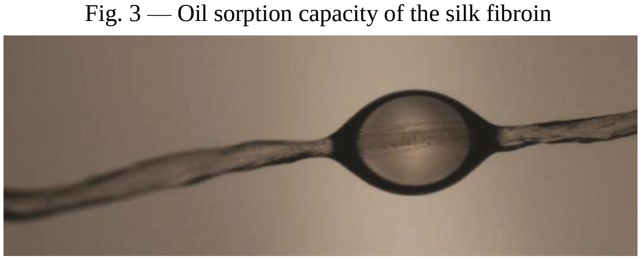

Fig. 4 — Oil droplet on chitosan coated silk fibroin

Further, it is observed that, the oil sorption capacity of chitosan coated and uncoated silk fibroin against engine oil is higher than the diesel oil. The difference in oil sorption ability of the sorbent to different oils is mainly due to the different oil adhesiveness ability between fibres and oils. Adhesiveness ability of high viscous oil towards fibre is, in general, higher than the low viscous oil[16]. Apart from oil viscosity, inherent density difference along with the likely polarity of asphaltenic compounds (asphaltenes, resins) also influence the oil sorption capacity[17].

3.4 Oil Retention Performance

The oil retention performance during field application, handling operation and transfer is an important factor for sorbent evaluation[18]. The oil retention curve of chitosan coated silk fibroin (2.0% chitosan concentration) is shown in Fig. 5. Oil from the sorbent is allowed to drip for a particular duration and oil retention performance of the sorbent is measured. The oil retention curve is divided into three different stages. The first stage is the rapid resolution phase, the oil dripped out rate from the sorbent material is very high (0-60 s). The second stage is the slow resolution phase, here the rate of release of oil from the sorbent is considerably reduced (61-140 s). The third stage is the equilibrium stage after 140 s, here the oil in sorbent lean towards to come into a steady-state and this duration is much longer. From Fig.5, it is also noted that the amount of engine oil retained on chitosan coated silk fibroin after 240 s is 21.10 g/g, while those of diesel oil is 15.21 g/g, indicating the good retention capability. The improved affinity between sorbent and oil stabilizes the interaction force between chitosan coated silk fibroin and oil. Also the capillary pressure

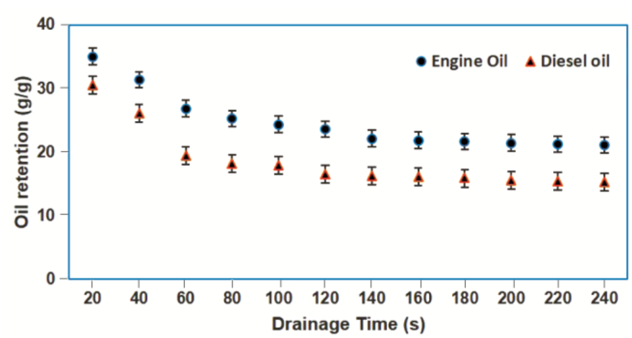

Fig. 5 — Oil retention curve of chitosan coated silk fibroin

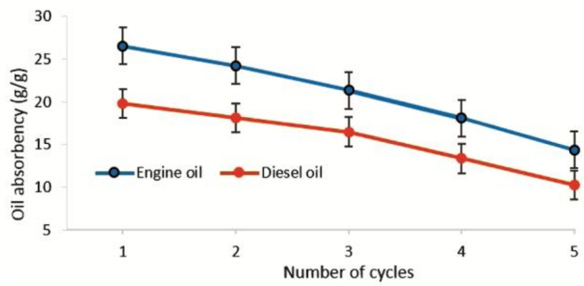

Fig. 6 — Reusability of chitosan coated silk fibroin

Table 1 — Comparison of oil sorption capacity of sorbents

Sorbent	Medium	Maximum sorption capacity (g/g)	References
Polypropylene	Engine oil	29.22	20
Polyester	Silicone oil	26.50	21
Silk fibroin	Engine oil	14.32	Present study
	Diesel oil	10.29	Present study
Chitosan coated silk fibroin	Engine oil	26.80	Present study
	Diesel oil	19.46	Present study

of the coated silk fibroin is found sufficient to hold the weight of the oil molecule retained in the sorbent matrix and chitosan coated layer. These findings are correlated with previous published data[18].

3.5 Reusability of Chitosan Coated Silk Fibroin

The absorbency of chitosan coated silk nonwoven fabrics against engine oil and diesel oil after five sorption cycles is shown in Fig. 6. The result reveals that the oil absorbency of chitosan coated silk nonwoven fabrics against both engine oil and diesel oil decreases after every cycle. The irreversible deformation of nonwoven structure, the contraction of inter-fibre spaces and the existence of residual oil in nonwoven structure are all related to the reduction in oil absorbency[19]. Regardless of this, it is worth stating that even after 5 cycles, the oil absorbency of chitosan coated silk nonwoven fabrics is 14.39 g/g and 10.30 g/g against engine oil and diesel oil respectively; these values are found comparable to untreated silk nonwovens. Therefore, chitosan coated silk nonwoven fabrics could be reused several times without noticeable loss of effectiveness, signifying its potential as an oil sorbent for recovering most of liquid oil through simple squeezing.

3.6 Comparison of Oil Sorption Capacity of Sorbents

A comparison of oil sorption capacity of silk fibroin, chitosan coated silk fibroin and polypropylene and polyester is shown in Table 1. It is observed that the sorption capacities of chitosan coated silk fibroin is comparable to polyester and lower than polypropylene. However, use of the chitosan coated silk fibroin as sorbent for oil spill removal is sustainable, has a low energy demand & low carbon footprint, and is very clean compared to synthetic oil sorbents currently in use. At the end of life cycle, when oil sorbent based on chitosan coated silk fibroin turn out to be a waste product, it may be used as a high energy fuel, due to the emission of very low toxic fumes when subjected to burning. Hence, chitosan coating on silk fibroin can be a novel method to develop ecofriendly sorbent for oil spill removal applications.

4 Conclusion

In this work, novel oil sorbent has been developed by coating of chitosan onto silk fibroin. The effect of chitosan coating on oil sorption and oil retention behavior of silk fibroin is studied. The maximum oil sorption capactiy of chitosan coated silk fibroin is 26.80 g/g and 19.46 g/g for engine oil and diesel oil respectively. Reusability test results suggest that after 5 cycles, the oil absorbency of chitosan coated silk fibroin is 14.39 g/g and 10.30 g/g against engine oil and diesel oil respectively. Use of chitosan coated silk fibroin as sorbent for oil spill removal is sustainable, has a low energy demand & low carbon footprint, and is very clean compared to synthetic oil sorbents currently in use. Finally, chitosan coating on silk fibroin can be a novel method to develop ecofriendly sorbent for oil spill removal applications.

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